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do hereby verify that I am fully conversant with the Japanese and English languages and that attached translation signed by me is, to the best knowledge and belief, a true and correct English translation of the Japanese Patent Application No. 2000-94233.

DATED June 18, 2003

SIGNED T. Kodaira

PATENT OFFICE

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This is to certify that the annexed is a true copy of the following application as filed with this office.

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[TITLE OF THE INVENTION] Lithium Secondary Battery

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[Title o the Invention] Lithium Secondary battery

[Scope of the Claim for Patent]

[Claim 1]

A lithium secondary battery comprising:

an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution,

characterized in that one side of the battery has a pressure release hole which is positioned at a center of a electrode cap.

[Claim 2]

The lithium secondary battery according to claiml, characterized in that said winding core is disposed at a center axis of said battery.

[Claim 3]

The lithium secondary battery according to claim 1 or 2, wherein said pressure release hole is unified with an external electrode which does not prevent the hole from releasing pressure.

[Claim 4]

A lithium secondary battery comprising:

an internal electrode body formed by winding a positive electrode plate, and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution,

characterized in that one side of the battery has a pressure release hole which is positioned at the center of a electrode cap, and said pressure release hole is made on only one electrode cap on both sides of the battery.

[Claim 5]

The lithium secondary battery comprising:

an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution,

characterized in that a pressure release hole is formed at a electrode cap on one side of the battery, and said pressure release hole has a pressure release valve sealed by an elastic body and a metal foil being brought into pressure contact with a spacer.

[Claim 6]

The lithium secondary battery according to claim 5, characterized in that said metal foil is formed so as to have a surface pressure of not less than 980 kPa.

[Claim 7]

The lithium secondary battery according to claim 5 or 6, characterized in that said spacer is formed with a metal material having a Young's modulus not less than 170 Gpa.

[Claim 8]

The lithium secondary battery according to any one of claim 5 to 7, characterized in that said spacer is a ring member or a ring member having stopper structure in order that a

stress not less than a constant amount will not be applied to said elastic body.

[Claim 9]

The lithium secondary battery as claimed in any one of claims 5 to 8, characterized in that said metal foil is mainly made of Al, Cu, or Ni that is coated by a fluoride resin.

[Claim 10]

The lithium secondary battery as claimed in any one of claims 5 to 10, characterized in that a stress applied to said elastic body is not less than 980 kPa and not more than a stress to cause the elastic body to maintain elasticity maintenance percentage of not less than 95%.

[Claim 11]

The lithium secondary battery as claimed in any one of claims 5 to 10, characterized in that said elastic body is a packing processed in advance to a predetermined size.

[Claim 12]

The lithium secondary battery as claimed in any one of claims 5 to 11, characterized in that said packing is made of any one of ethylene propylene rubber, polyethylene, polypropylene or fluoride resin.

[Claim 13]

A lithium secondary battery comprising;

an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution,

characterized in that one side of the battery has a pressure release hole which is positioned at a center of a electrode cap, and the pressure release hole has a pressure release valve sealed by an elastic body and a metal foil being brought into pressure contact with a spacer.

[Claim 14]

A lithium secondary battery comprising:

an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution,

characterized in that the pressure release hole is commonly used as an electrolyte solution inlet.

[Claim 15]

A lithium secondary battery comprising:

an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution,

characterized in that an electrode cap on one side of the battery are formed in approximately rotary symmetry around the center axis of the winding core of the internal electrode body being a center.

[Claim 16]

The lithium secondary battery as claimed in any one of claims 1 to 15, characterized by having a electrode capacity of not less than 2 Ah.

[Claim 17]

The lithium secondary battery as claimed in any one of claims 1 to 16, characterized by being a battery to be mounted on vehicles.

[Claim 18]

The lithium secondary battery according to claim 17, characterized in that the battery is to be mounted on an electric vehicle or a hybrid electric vehicle.

[Claim 19]

The lithium secondary battery according to claim 17, characterized in that the battery is for an engine starter.

[Claim 20]

A method of manufacturing a lithium secondary battery comprising:

providing an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution,

preparing a plate-like member functioning as a cap after production, an elastic body, a metal foil and a spacer which are processed in advance to a predetermined size; disposing said elastic body and said metal foil in a predetermined position; combining them with said spacer to form a pressure release hole unit; and fitting said pressure release hole unit into said plate-like member to produce electrode caps.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a lithium secondary battery which is simple and superior in productivity, safety in operation and reliability.

[0002]

[Prior Art]

In recent years, a lithium secondary battery is widely used as a small secondary battery with high energy density for electronic equipment such as portable communication equipment and a notebook-sized personal computer. In addition, demands for resource saving and energy saving are raised on the background of international protection of the earth environment, among the automobile industry, the lithium secondary battery is being developed as a motor driving battery for an electric vehicle and hybrid electric vehicle. In addition, among the electric power industry, the lithium secondary battery is expected as a power storage apparatus during the night for the efficient use of energy, and an early realization of the lithium secondary battery with large capacity, suitable for such purpose becomes the center of the public.

[0003]

A lithium secondary battery uses lithium transition metal compound oxides, etc., as a positive active material, on the other hand, for the negative active material, carbonaceous material such as hard carbon and black carbon, etc., is used. During charging, a lithium ion of the positive

active material is transferred through an electrolyte solution in which a lithium ion electrolyte is dissolved in an organic solvent, to and captured by the negative active material. And during discharging, a reverse battery reaction take place.

[0004]

Although the lithium secondary battery is capable of charging and discharging in this manner, it has higher operating voltage and higher energy density than the conventional lead storage battery etc., it has various safety apparatus inside in order to prevent the accident during charging and discharging. For example, over-discharging due to a short circuit of external terminals, rapid charging or over-charging due to malfunction of a charging device, and adding the reversal voltage caused by the misusage of users to connect opposite side, it requires a pressure release valve as a safety apparatus.

[0005]

[Problems to be Solved by the Invention]

Such a lithium secondary battery has a pressure release hole as a pressure release valve, which is a security device in order to prevent the burst of the battery. As shown in Fig. 2, it is generally separated from an external terminal. In case of the lithium secondary battery for hybrid electric vehicle and the like, it requires so large current that it is preferable to connect the batteries in series, and the external terminal is positioned at the center of the electrode

cap. Therefore, the pressure release hole is positioned at the side of the electrode cap apart from the center.

[0006]

This pressure release hole is a part of the safety mechanism in order to prevent from the burst as the remark above mentioned, it is necessary to be able to control the opening pressure at the moment of rising of the pressure inside the battery. And it is preferable to be simple in structure, easy in assembly and superior in pressure release operation. Therefore, the inventors disclosed in Japanese Patent Application No. Hei 11-341741, about a pressure release hole made by bending a projection near the pressure release hole and caulking with metal foil via a spacer. Although the pressure release hole is simple in structure and superior in pressure release operation compared with conventional pressure release hole, further improvement in operation process are still expected to change the components for the sake of the workability in assembly process.

[0007]

And commonly, operation of the electrolyte solution inpouring is taken place before attaching the electrode cap on the battery case, and electrolyte solution is poured from the top of the internal electrode body as shown in Fig. 3. In this operation, it takes a long time for the impregnation of the electrolyte solution, and that causes the loss of the electrolyte solution due to evaporation of some organic solvents in the electrolyte solution during the impregnation,

and results in the problems like the change of the electrolyte concentration. In order to solve such kinds of problems, inventors formerly created an inlet for the electrolyte solution on the electrode cap, that enable the method of pouring the electrolyte solution with the nozzle after the attachment of the electrode cap, which is disclosed in Japanese Patent Application No. Hei 10-290832. In this case, the external electrode and the inlet of the electrolyte solution are combined into the structure of the electrode terminal, with a pressure release hole as an another part.

Even such a structure requires two holes for the inlet of the electrolyte solution and the pressure release hole, so the area of the portions to be sealed will become large, giving rise to aptness of leakage of the electrolyte solution.

[0008]

In addition, low cost case with anti-burst safety mechanism using compression bonding is disclosed in Japanese Patent Laid-Open No. 11-49217. However, it doesn't disclose any solving means such as particular shapes of components of the anti-burst safety mechanism and a fixing pressure at the time of assembly and therefore was not sufficiently satisfactory for the use of the electric vehicle and the like which demands sophisticated safety mechanism.

[0009]

[Means to Solve the Problem]

This invention is considered specifically for the problems and improvements on above mentioned prior art, and

the purpose of this invention is to provide a lithium secondary battery with simpler structured pressure release valve and electrode cap, which is cost effective and securing the reliability. Furthermore, the purpose of this invention is to provide a lithium secondary battery, which is superior in reliability and easy to manufacture by reducing the area of the hole by way of using the pressure release hole as the inlet of the electrolyte solution.

[0010]

Namely, according to this invention, there is provided a lithium secondary battery comprising, an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution, characterized in that one side of the battery has a pressure release hole which is positioned at the center of a electrode cap.

[0011]

It is preferable for the lithium secondary battery in this invention that said winding core is positioned at the center of the battery. It is also preferable for it that said pressure release hole has a united structure with an external terminal, which has a structure unresisting the pressure release.

[0012]

Moreover, there is provided a lithium secondary battery comprising, an internal electrode body formed by winding a

positive electrode plate, and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution, characterized in that one side of the battery has a pressure release hole which is positioned at the center of a electrode cap, and said pressure release hole is made on only one electrode cap on both sides of the battery.

[0013]

Furthermore, in the lithium secondary battery of this invention, there is provided a lithium secondary battery comprising an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution, characterized in that a pressure release hole is formed at a electrode cap on one side of the battery, and said pressure release hole has a pressure release valve sealed by an elastic body and a metal foil being brought into pressure contact with a spacer.

[0014]

In the lithium secondary battery of the present invention, the metal foil is preferably formed so as to have the surface pressure of not less than 980 kPa. Control on this surface pressure leads to secure the battery's air-tightness. The spacer is preferably formed with a metal material having a Young's modulus not less than 170 GPa, and is preferably a ring member having stopper structure in order that the stress not less than a constant amount will not be applied to the ring

member or the above described elastic body. Moreover, the metal foil is preferably mainly made of Al, Cu or Ni respectively that is coated by a fluoride resin.

[0015]

The pressure contact force applied to the elastic body is preferably not less than 980 kPa and not more than the force amount to cause the elastic body to maintain elasticity maintenance percentage of not less than 95%, and the elastic body is preferably a packing processed in advance to a predetermined size. In particular, the elastic body is preferably made of ethylene propylene rubber, polyethylene, polypropylene or fluoride resin.

[0016]

Furthermore, according to the present invention, there is provided a lithium secondary battery comprising, an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution, characterized in that one side of the battery has a pressure release hole which is positioned at a center of a electrode cap, and the pressure release hole has a pressure release valve sealed by an elastic body and a metal foil being brought into pressure contact with a spacer.

[0017]

Moreover, in this invention, there is provided a lithium secondary battery comprising, an internal electrode body

formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution, characterized in that the pressure release hole is commonly used as an electrolyte solution inlet.

[0018]

In addition, in this invention, there is provided a lithium secondary battery comprising, an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution, characterized in that an electrode cap on one side of the battery are formed in approximately rotary symmetry around the center axis of the winding core of the internal electrode body being a center.

[0019]

The lithium secondary battery of the present invention is suitable to a battery with the electrode capacity of not less than 2 Ah. The present invention can be suitably used as a battery to be mounted on vehicles, and for an engine starter, and moreover can be suitably used for a battery for driving a motor of an electric vehicle or a hybrid electric vehicle.

[0020]

In addition, according to the present invention, there is provided a method of manufacturing a lithium secondary battery comprising, providing an internal electrode body

formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of a winding core and dipped into nonaqueous electrolyte solution, preparing a plate-like member functioning as a cap after production, an elastic body, a metal foil and a spacer which are processed in advance to a predetermined size; disposing said elastic body and said metal foil in a predetermined position; combining them with said spacer to form a pressure release hole unit; and fitting said pressure release hole unit into said plate-like member to produce electrode caps.

[0021]

[Mode for Carrying out the Invention]

A lithium secondary battery in this invention uses a pressure release valve as a security mechanism for preventing the burst of the battery, and by simplifying a structure of the pressure release valve and an electrode cap, and also by using a pressure release hole having the pressure release valve as an inlet of the electrolyte solution. Therefor, the lithium secondary battery accomplished restraining a leakage of the electrolyte solution, simple manufacturing and improvement in reliability. As follows, embodiments of the present invention will be described, but it goes without saying that the present invention is not limited to the following embodiments.

[0022]

A lithium secondary battery in this invention has a pressure release hole 18 which is positioned at the center of

a electrode cap 15 on one side of the battery as shown in Fig. 1 and Fig. 5. At this time, a winding core 13 of an internal electrode body 1 is positioned at the center of the battery, and the pressure release hole 18 has a united structure with an external terminal 16 having a structure that does not prevent the hole from releasing pressure.

[0023]

According to a lithium secondary battery, generally an internal electrode body is positioned at the center of the battery, in case of using a cylindrical internal electrode body 1, as a matter of course said winding core 13 is positioned at the center of the electrode cap 13. In this case, the position of the pressure release hole is disposed in the center of the electrode cap 15 so that the pressure release hole 18 can be structured in an integrated fashion easily for the pressure release hole 18 together with its external terminal 16 as shown in Fig. 1. In order to integrate the external terminal with the pressure release hole, the pressure release valve provided at the pressure release hole must be realized to have a structure that is simple and has pressure release operation performance so as to be contained inside the external terminal. The present invention is the one that has realized this object and simplified the structure of the electrode cap as a whole.

[0024]

Further, in the present invention, one side of the battery has a pressure release hole which is positioned at the

center of a electrode cap, and the pressure release hole is made on only one electrode cap on both sides of the battery.

[0025]

In conventional lithium secondary batteries, pressure release holes are made on each electrode cap on both sides of the battery in order to prevent the burst of the battery in case that high internal pressure, such that the battery is broken is generated. This is because as the conventional pressure release hole is positioned not at the center of but at the side of the electrode cap, internal pressure of the battery can not easily be released.

[0026]

However, as described in the lithium secondary battery of the present invention, the winding core 13 which is a cavity of an internal electrode body is positioned at the center of the battery, and the pressure release hole 18 is disposed on outer areas 32, 33 of the winding core, and internal pressure of the battery can very quickly be released. Therefore, the pressure release hole made on only one of the electrode caps provided on both sides of the battery, can prevent the burst of the battery. Though conventionally pressure release holes 18 are made on each electrode cap 15 on both sides of the battery, only one pressure release hole is enough. Therefore, a structure of another electrode cap 15 which does not have pressure release hole 18 is simpler and its manufacturing cost can be reduced.

[0027]

In addition, in the present invention, the pressure release hole 18 is positioned at the center of the electrode cap 15 and, as described later the pressure release hole 18 is commonly used as an electrolyte solution inlet. This structure enables to short injection of an electrolyte solution and to reduce a loss of the electrolyte solution, and further since this structure can reduce the hole area of the battery it enables to reduce leakage of the electrolyte solution.

[0028]

Additionally, in a lithium secondary battery in this invention, a pressure release hole 18 is formed at the center of a electrode cap 15 on one side of the battery, and the pressure release hole 18 has a pressure release valve 20 sealed by a metal foil 19 being brought into pressure contact with a spacer 26 via an elastic body 17, as shown in Fig. 1 and Fig. 5. In this case, the metal foil 19 is preferably formed so as to have the surface pressure of not less than 980 kPa. Control on this surface pressure leads to control on the pressure contact force toward each component of the pressure release valve 20, and actually since the metal foil 19 seals the pressure release hole, its air-tightness will become securable.

[0029]

A lithium secondary battery for a hybrid electric vehicle and the like releases a large current and the like, and therefore, the battery temperature might increase and the

interior of the battery could be excessively highly pressurized and therefore, a high-performance pressure release valve will become necessary. The temperature is low around –40℃ when the lithium secondary battery of the present invention is actually used, and therefore, also for the pressure release valve, each property of components of a spacer, an elastic body, and a metal foil as well as the pressure release valve's function as a whole under working temperature of the lithium secondary battery will become a problem.

[0030]

Under the circumstances, in the present invention, the spacer is preferably formed with a metal material having a Young's modulus not less than 170 GPa under the temperature described above. This is for avoiding the spacer 26's expansion and contraction refraining from applying sufficient pressure to the elastic body 17 as well as the metal foil 19 at the time when pressure contact and fixing are implemented with pressure insertion of the spacer 26.

[0031]

Moreover, a spacer is preferably a ring member 26A or a ring member 26B having stopper structure in order that the stress not less than a constant amount will not be applied to the elastic body. The electrode cap 15 is, as shown in Fig. 5, designed so that a spacer is pressed for insertion with an angle from the upper portion of the pressure release hole 18 to the lower portion thereof to bring the elastic body as well

as the metal foil into pressure contact and fixing and an appropriate surface pressure is applied to the metal foil. In addition, as shown in Fig. 6, the reason why the spacer 26B comprises a stopper structure is for making it sure that the spacer shall not be pushed into inside the pressure release hole to a degree not less than necessary and no pressure to an excess degree shall applied to the elastic body and the like to be broken.

[0032]

These spacers, which are shaped as rings, are further preferably given a curvature processing at the internal edge portion of the spacers in order to maintain the function of the elastic body as well as the metal foil being the adjacent components without damaging them. In this case, if the curvature radius at the internal edge portion of the spacer is not less than 30 μm which is not more than a half of the spacer's thickness, the function of the pressure release hole can be maintained without any problems.

[0033]

In addition, in the present invention, for the metal foil 19, the one made of mainly Al, Cu, or Ni that are coated by the fluoride resin are suitably used. The metal foil 19, which will be brought into direct contact with electrolyte solution, is the preferably highly pure one excellent in anti-corrosion against electrolyte solution for use, and the metal foil 19 having surfaces coated with fluoride resin

should be used so that the one in which improvement in tolerance is planned and excellent in safety.

[0034]

Moreover, in the present invention, the pressure contact with a spacer is preferably conducted, so that the stress applied to the elastic body is not less than 980 kPa and not more than the force amount to cause the elastic body to maintain elasticity maintenance percentage of not less than 95%. This enables the surface pressure of the metal foil 19 to be secured and the air-tightness to be maintained so that leakage of the electrolyte solution is prevented

[0035]

As the elastic body 17, an elastic body processed in advance to a predetermined size, that is, a packing is preferably used, and as materials in particular, ethylene propylene rubber, polyethylene, polypropylene or fluoride resin are nominated. These resins are excellent in anticorrosion, and even if the nonaqueous electrolyte solution containing an organic solvent of an ester system is used, reliability is secured.

[0036]

As the elasticity maintenance percentage of the elastic body is expressed by changes in thickness before and after the pressure contact force has been applied with an autograph to an elastic body of 'for example' the outer diameter of 10 mm $\phi\times$ the inner diameter of 7 mm$\phi\times$1 mm, that is, when the pressure contact force is released after a predetermined time

lapses. That is, the elasticity maintenance percentage D of the elastic body is given by $D=B_1/A_1 \times 100$ with A_1 being thickness of the elastic body prior to application of the pressure contact force and B_1 being thickness of the elastic body after application of the pressure contact force.

[0037]

In case that the elasticity maintenance percentage is not less than 95%, the elasticity is secured as well as the surface pressure is secured. On the other hand, it is necessary to insert a metal spacer under pressure in order that such a stress that no leakage will take place from the pressure release hole 18 with or under the pressure which operates the pressure release valve 20,. is applied to the elastic body. 980 kPa is a rough standard of operating pressure of the pressure release valve 20.

[0038]

Fig. 4(a) to 4(d) are graphs describing the elasticity maintenance percentage and the displacement by way of relationship with the applied stress force with regard to the respective elastic bodies (Fig. 4(a): ethylene propylene rubber, Fig. 4(b): fluoride resin, Fig. 4(c): polyethylene, and Fig. 4(d): polypropylene) each of which has been processed to the outer diameter of 10 mm$\phi \times$ the inner diameter of 7 mm $\phi \times$1 mm, and the shaded frame portions shown in respective drawings are the suitable ranges related to the above described present invention, and are the regions where good surface pressure can be obtained.

[0039]

Next, the pressure release valve 20 disposed in the above described electrode cap 15A will be described in detail. Fig. 5 is an enlarged sectional view showing the structure of the pressure release valve 20 shown in Fig. 1. The pressure release valve 20A is configured by comprising a metal foil, an elastic body, and a ring-form metal spacer from the lower portion of the electrode cap. This is a basic configuration in the present invention, but also in this case, the electrode cap is inclined with a degree, and in order to control the deformation amount of the elastic body homogeneously, the stopper portion 27A is provided to the electrode cap 15A so that the spacer 26A is not structured to be pushed into the side of the elastic body 17A in not less than a predetermined amount. This serves to make it possible that the appropriate stress to the elastic body and the necessary surface pressure of the metal foil is secured and the air tightness of the pressure release valve 20A is maintained. At this occasion, the metal spacer is further preferably fixed with an adhesive agent 28 in order to secure air tightness firmly also under a low temperature to be used. For this adhesive agent, an aerobic adhesive agent is suitably used.

[0040]

Another embodiment of the pressure release valve is shown in Fig. 6. The pressure release valve 20B is configured by comprising a metal foil, the elastic body, and a ring-form metal spacer having stopper structure in order from the lower

portion of the electrode cap. This is the one in which the surface pressure applied to the metal foil 19 is controlled more firmly so as to enhance its function as a pressure release valve. That is, the present invention is under the state that the packing being an elastic body is pressured and flattened, or stress is being applied to the elastic body all the time, and if it is applied to an excess degree, elasticity will be gone and function as the pressure release valve as a whole will be lost. Therefore, a reception portion on the stress has been created so that the stress has been controlled to not more than a predetermined amount more firmly.

[0041]

Another embodiment of the pressure release valve is shown in Fig. 7. The pressure release valve 20C is configured by comprising the elastic body, a metal foil, and a ring-form metal spacer having stopper structure in order from the lower portion of the electrode cap. Thus, configuration by comprising the metal foil 19 sandwiched between the elastic body 17C and the metal spacer 26C is realizable, and this combination, as shown in Fig. 8, enables the respective components of the pressure release valve to be integrated in advance as a pressure release hole unit 29.

[0042]

Namely, in the lithium secondary battery of this invention, an elastic body, a metal foil and a spacer which are processed in advance to a predetermined size, and the above described elastic body and the above described metal foil are

disposed in a predetermined position, and are combined with the spacer to form a pressure release hole unit, and then an electrode cap is produced by fitting the pressure release hole unit into a plate-like member functioning as a cap after production. This serves to make it possible to complete the pressure release hole18c by only fitting the pressure release hole unit 29 into the electrode cap 15c.

[0043]

In the case where the above described pressure release valves 20A, 20B, and 20C are used, for any of the cases, in the state of the single body of the electrode cap 15 prior to assembly of the battery, with only the metal foil and the elastic body being mounted, and with the metal spacer being inserted by pressure and the like the pressure release hole 18 comprising the pressure release valves 20A, 20B, and 20C having pressure release operating nature can be formed to make it possible to attain excellent effects such as further reduction in equipment costs, simplification of assembly work, and improvement in manufacturing yield factor.

[0044]

Further, in the lithium secondary battery of the present invention, as shown in Fig. 1 and Fig 5, one side of the battery has a pressure release hole 18 which is positioned at the center of a electrode cap 15, and the pressure release hole 18 has a pressure release valve 18 sealed by an elastic body 17 and a metal foil 19 being brought into pressure contact with a spacer 26. In addition, in the lithium secondary battery of

the present invention, the pressure release hole can be commonly used as an electrolyte solution inlet.

[0045]

That is, this invention provides an excellent pressure release valve 18 in which a simple structured pressure release hole is integrated with the external terminal and is disposed at the center of the electrode cap, and moreover the internal electrode body' winding core is disposed at the center of the battery so that the electrolyte solution can be injected with that pressure release hole.

[0046]

In this invention, as for that electrolyte solution injection method, as shown in Fig. 9, the one uses the pressure release hole as the electrolyte solution inlet prior to sealing the pressure release hole with a pressure release valve and implements by inserting the electrolyte solution injection nozzle 25 into a penetrated hole of the winding core 13. Adoption of this method serves to make it possible to insert the tip of the electrolyte solution injection nozzle 25 into the other end of the battery 14 so that the electrolyte solution is injected well.

[0047]

The battery 14 is disposed in the space such as a globe box and the like where atmosphere can be adjusted, when the electrolyte solution is injected. When the interior of the globe box, etc. is made to be vacuumed atmosphere with a vacuum pump, the battery 14 is in a state that the pressure release

hole used in common as an electrolyte inlet is open, and therefore the interior of the battery 14 will be vacuum atmosphere. Here, the vacuum level is preferably made to be the state of vacuum higher than around 0.1 torr (13.3 Pa).

[0048]

Under this state, the tip of the nozzle 25 is inserted through the electrolyte inlet 31, and subsequently through the penetrated hole 34 of the winding core 13 to reach the position of the end surface of the internal electrode body 1 in the bottom side of the battery, that is, the position indicated by the broken line AA' in Fig. 9, and thereafter the electrolyte solution is injected until the internal electrode body 1 is dipped, that is, to the position indicated by the broken line BB' in Fig. 9. Here, insertion of tip of the nozzle 25 to reach the lowest portion(cap 15) inside the battery 14 can prevent the electrolyte solution from splashing so as to start dipping into the electrolyte solution the internal electrode body 1 from the end surface of the bottom surface portion without fail.

[0049]

Incidentally, during the dipping process of the electrolyte solution, the vacuum level is preferably maintained approximately in such a degree that the electrolyte solution will not boil, and the vacuum level at this time largely depends on the nature of the solvent composing the electrolyte solution being used. In addition, as the material quality for the injection nozzle 25, metals or resins which

will not undergo corrosion by the electrolyte solution are used, and the injection nozzle 25 is connected with the electrolyte reserve tank disposed outside the globe box, etc. via a tube or a pipe, etc. so that the electrolyte solution is transported from the electrolyte reserve tank with a quantitative pump, etc.

[0050]

Thus, the battery 14 is filled with the electrolyte solution from the lower portion so that the internal electrode body 1 is dipped from the lower portion to the upper portion, the bubble generated from the internal electrode body 1 can come out through the space which is not dipped into the electrolyte solution, dipping by the electrolyte solution will be able to be implemented efficiently. Thus, injection time of the electrolyte solution can be shortened, and in this case, even in the case where a highly volatile solvent is contained in the electrolyte solution, its evaporation quantity can be suppressed to the smallest limit so as to prevent the electrolyte solution's performance from dropping.

[0051]

In addition, the lithium secondary battery of the present invention is a lithium secondary battery, which has an internal electrode body formed by winding a positive electrode plate and a negative electrode plate via a separator on an outer periphery wall of the winding core and dipped into nonaqueous electrolyte solution as shown in Fig. 1 and Fig. 10, and the electrode cap on one side of the battery, are

configured to be formed in approximately rotary symmetry around the center axis of the winding core of the internal electrode body.

[0052]

In this invention, if the electrode cap has a pressure release hole in a position of corresponding with the center of the electrode cap, the pressure release hole is structured to be integrated with the external terminal, and the pressure release hole is used in common as the electrolyte solution inlet, as shown in Fig. 10(a), the electrode cap will be able to be formed in approximately rotary symmetry around the center axis of the winding core of the wound type internal electrode body.

[0053]

In the lithium secondary battery, in order to accelerate penetration of the solution into the internal electrode body in the injection operation of the electrolyte solution, the electrolyte solution might be poured from the upper portion of the internal electrode body. In this case, as shown in Fig. 10(b), the electrode cap preferably has a slits 30 formed by providing slits in the internal electrode portion. The number of these slits can, as shown in Fig. 10(c), 10(d), and 10(e), be provided corresponding with necessity, and there is no limitation on its number or position. Here, approximately rotary symmetry of the electrode cap in the present invention has a wide mean including complete rotary symmetry to the one in which a slit is formed as shown in Fig. 10(b).

[0054]

Since the electrode cap in the present invention is formed in rotary symmetry and thus rotary processing such as a lathe, etc. will be able to form the electrode cap with its rotary axis being the center, the manufacture will become easy and the processing costs can be largely reduced.

[0055]

The lithium secondary battery of the present invention is the one in which the pressure release valve is used as a safety mechanism for burst prevention of the battery. Accordingly, there is no limitation on other materials or battery structure. Main members comprising the battery and their structures will be generally described as follows.

[0056]

One of structures of the electrode body that can be referred to as the heart of the lithium secondary battery is the single cell structure as seen in a small-capacity coin cell in which each of positive and negative electrode active substances are press-molded into a disk form to sandwich a separator.

[0057]

In contrast with the small-capacity battery such as a coin cell, one of structures of the electrode body to be used for a large-capacity battery is a wound type. As shown in the perspective view of Fig. 11, a wound-type electrode body 1 is configured by winding a positive electrode plate 2 and a negative electrode plate 3 through separator 4 of porous

polymer around the outer periphery of the winding core 13 so that the positive electrode plate 2 and the negative electrode plate 3 are not brought into direct contact with each other. The number of lead lines 5 and 6 attached to the positive electrode plate 2 and the negative electrode plate 3 (hereinafter to be described as “electrode plates 2 and 3”) may be at least one, and a plurality of lead lines can make electricity collection resistance small.

[0058]

As another structure of the electrode body, a lamination type, which is configured by laminating a plurality of layers of single cell type electrode bodies used for coin, is nominated. As shown in Fig. 12, a lamination-type electrode body 7 is the one comprising a positive electrode plate 8 and a negative electrode plate 9 both having predetermined forms and a separator 10, the positive electrode plate 8 and the negative electrode plate 9 being laminated through the separator alternately, and at least one electrode lead 11 or 12 is attached to one sheet of electrode plates 8 and 9. Materials to be used, and the producing method, etc. for the electrode plates 8 and 9 are similar to those in the electrode plates 2 and 3, etc. for the wound-type electrode body 1.

[0059]

Next, with the wound-type electrode body 1 as an example, its configuration will be described further in detail. The positive electrode plate 2 is produced by applying positive active substance onto the both surfaces of the electricity

collection substrate. As the electricity collection substrate, a metal foil such as an aluminum foil or a titanium foil, etc., which is good in corrosion resistance against positive electrochemical reaction, is used, but other than foils, punching metal or mesh may be used. In addition, as the positive active substance, a lithium transition metal compound oxide such as lithium manganese oxide ($LiMn_2O_4$), lithium cobalt oxide ($LiCoO_2$), lithium nickel oxide ($LiNiO_2$) are suitably used, and preferably the carbon powder such as acetylene black and the like are added to these as conduction assistant agent.

[0060]

Coating of the positive active substance is implemented by applying to the electricity collection substrate and drying a slurry or a paste, which was produced by adding a solvent and bonding agent, etc. to the powdered positive active substance, and thereafter corresponding with necessity, press processing, etc. is implemented.

[0061]

The negative electrode plate 3 can be produced similarly as in the positive electrode plate 2. As the electricity collection substrate of the negative electrode plate 3, copper foil or nickel foil, etc., which is good in corrosion resistance against negative electrochemical reaction, is suitably used. As the negative active substance, an amorphous carbon material such as soft carbon or hard carbon,

or carbon powder such as artificial graphite, natural graphite or highly graphitized carbon material are used.

[0062]

As the separator 4, it is suitable to use a three-layer structural material in which a polyethylene film (PE film) having Li+ permeability and including micropores is sandwiched between porous polypropylene films (PP films) having Li+ permeability. This serves also as a safety mechanism in which when the temperature of the electrode body is raised, the PE film is softened at about 130℃ so that the micropores are collapsed to suppress the movement of Li+, that is, the battery reaction. And, when the PE film is sandwiched between the PP films having a softening temperature higher than that of the PE film, the PP films maintain their original shape even if the PE film is softened, thereby preventing the contact/short-circuit between the positive electrode plate 2 and the negative electrode plate 3 so as to enable certain suppression of the battery reaction and reservation of safety.

[0063]

At the time of winding operation on these electrode plates 2 and 3 and the separator 4, the electrode leads 5 and 6 are respectively attached to the portions where the electricity collection substrates are exposed without any electrode active substances being applied onto the electrode plates 2 and 3. For the electrode leads 5 and 6, foil-like ones made of the same quality as for the electricity collection substrate of the respective electrode plates 2 and 3 are

suitable used. The electrode leads 5 and 6 can be attached to the electrode plates 2 and 3 by ultrasonic welding or spot welding, etc. At this time, as shown in Fig. 11, attachment of the respective electrode leads 5 and 6 is carried out so that the electrode lead of one of the electrodes is disposed in one end surface of the electrode body 1, and thus contact between the electrode leads 5 and 6 can be prevented, which is preferable.

[0064]

For assembly of the battery, at first, conductivity between the terminals to extract currents to outside and the electrode leads 5 and 6 is secured while the produced electrode body 1 is inserted into the battery case and is held in a stable position. Thereafter, after they are dipped by the nonaqueous electrolyte solution, the battery case is sealed, and thus the battery is produced.

[0065]

Next, the nonaqueous electrolyte solution to be used in the lithium secondary battery of the present invention will be described. As a solvent, a single solvent or a mixture solvent of ester system ones such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and propylene carbonate (PC), γ-butyrolactone, tetrahydrofuran, and acetonitrile, etc., are suitably used.

[0066]

As the lithium compound to be dissolved into such solvent, that is, an electrolyte, lithium fluoride complex

compound such as hexafluoride lithium phosphate ($LiPF_6$), lithium fluoborate ($LiBF_4$), etc. or lithium halide such as lithhium perchlorate ($LiClO_4$) is nominated, and one or more kinds are dissolved into the above described solvent for use. In particular, it is preferable that LiPF6 which hardly causes oxidation decomposition and involves electrolyte solution with high conductivity.

[0067]

So far, the present invention is an invention in a lithium secondary battery using the wound-type electrode body, but it goes without saying that the present invention will not concern about battery structures other than that. Other configuring conditions of such a lithium secondary battery of the present invention are suitably adopted for the one with the electrode capacity of not less than 2 Ah. In addition, it goes without saying that there will be no limitation on use of the battery, which, however, can be suitably used in particular for the engine starter, and for driving a moter of electric vehicles or hybrid electric vehicles as a large capacity battery to be mounted on vehicles requiring a large current discharge.

[0068]

[Effect of the Invention]

As having been described so far, according to the lithium secondary battery of the present invention, since the structure of the pressure release hole become simplified, the pressure release hole with the pressure release valve can be

integrated with the external terminal, so that the structure of the electrode cap can be simplified. Further, the internal pressure is easily released from the pressure release hole, and accordingly, the pressure release hole is enough to be made on only one of the electrode caps provided on both sides of the battery.

Additionally, the pressure release hole is commonly used as an electrolyte solution inlet and an injection method of an electrolyte solution with using a nozzle is adopted. This enables to short injection of an electrolyte solution and to reduce a loss of the electrolyte solution. Further, since the injection of the electrolyte solution can be conducted after the electrode cap is mounted on and caulked with the battery case, this structure can reduce the hole area of the electrode cap and it enables to effectively reduce leakage of the electrolyte solution.

In addition, since the electrode cap is formed in rotary symmetry and thus only a lathe, etc. will be able to form the electrode cap.

As a result, in a lithium secondary battery of the present invention, the manufacture will become easy and the processing costs can be largely reduced, and improvement in reliability can be accomplished.

[Brief Description of the Drawings]

Fig. 1 is a sectional view showing an embodiment of a lithium secondary battery of the present invention in which a wound-type electrode body is adopted.

Fig. 2 is a sectional view showing an embodiment of a lithium secondary battery in which a conventional wound-type electrode body is adopted.

Fig. 3 is an explanatory view showing an example of a conventional injection method of an electrolyte solution.

Fig. 4 is a graph describing the relationship of the elasticity maintenance percentage and the displacement with regard to the respective elastic bodies.

Fig. 5 is a sectional view showing an embodiment of structure of a pressure release valve suitably used for the lithium secondary battery of the present invention.

Fig. 6 is a sectional view showing another embodiment of structure of a pressure release valve suitably used for the lithium secondary battery of the present invention.

Fig. 7 is a sectional view showing a still another embodiment of structure of a pressure release valve suitably used for the lithium secondary battery of the present invention.

Fig. 8 shows a perspective view and a sectional view showing an embodiment of a component of a pressure release valve suitably used for the lithium secondary battery of the present invention.

Fig. 9 is a sectional view showing an electrolyte solution filling method and a form of an electrode cap of the lithium secondary battery of the present invention.

Fig. 10 is an illustrated view showing a structure of the electrode cap in the lithium secondary battery according to the present invention.

Fig. 11 is a perspective view showing structure of a wound-type electrode body.

Fig. 12 is a perspective view showing structure of a lamination-type electrode body.

[EXPLANATION OF NUMBER]

1...wound-type electrode body, 2...positive electrode plate, 3...negative electrode plate, 4...separator, 5...tab (lead line), 6...tab, 7...lamination-type electrode body, 8...positive electrode plate, 9...negative electrode plate, 10...separator, 11...tab, 12...tab, 13...winding core, 14...battery, 15...electrode cap, 16A...positive electrode external terminal, 16B...negative electrode external terminal, 17...elastic body, 18...pressure release hole, 19...metal foil, 20...pressure release valve, 21...caulking portion, 22...internal terminal, 23...insulating polymer film, 24...battery case, 25...injection nozzle, 26...spacer, 27...stopper portion, 28...adhesive, 29...pressure release hole unit, 30...slit, 31...electrolyte solution inlet, 32,33...outer areas of winding core, 34...penetrated hole.

[NAME OF DOCUMENT] Abstract

[Abstract]

[Theme]

There is provided a lithium secondary battery which is manufacturing thereof become easy and is superior in safety, and is superior in reliability.

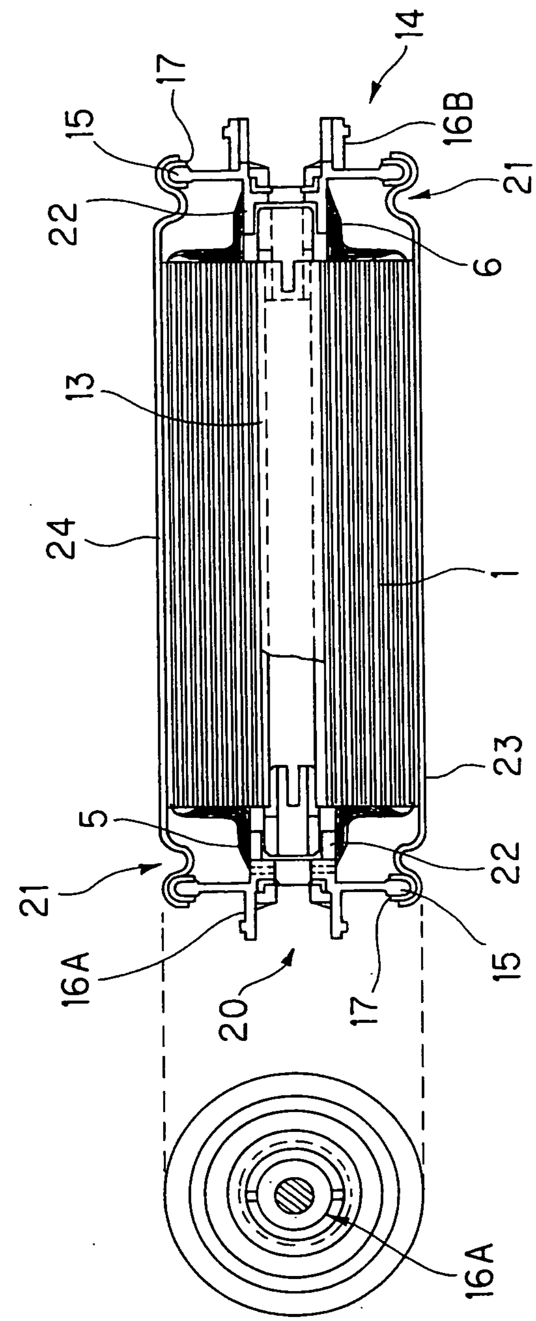
[Means]

The lithium secondary battery includes, an internal electrode body 1 formed by winding a positive electrode plate 2 and a negative electrode plate 3 via a separator 4 on an outer periphery wall of a winding core 13 and dipped into nonaqueous electrolyte solution. A pressure release hole 18, which is commonly used as an electrolyte solution inlet, is formed at a electrode cap 15A on one side of the battery 14, and the pressure release hole 18 has a pressure release valve 20 sealed by an elastic body 17 and a metal foil 19 being brought into pressure contact with a spacer 26.

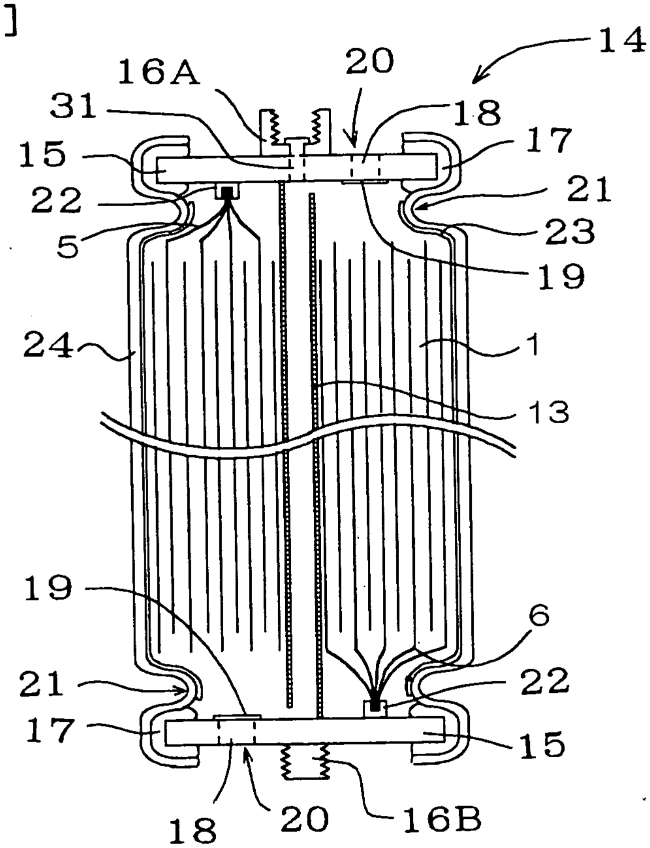
[Adopted Figure] Fig. 1

[Name of Document] Drawings

[Fig.1]



[Fig.2]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16A
20
31
18
15
17
22
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19
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13
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6
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18
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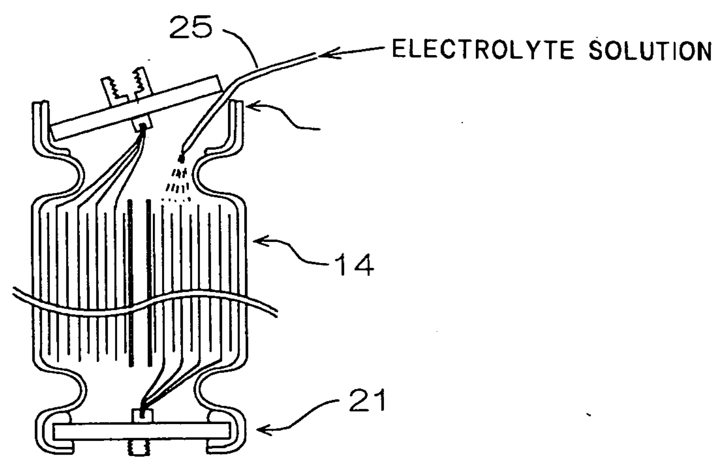
16B

[Fig.3]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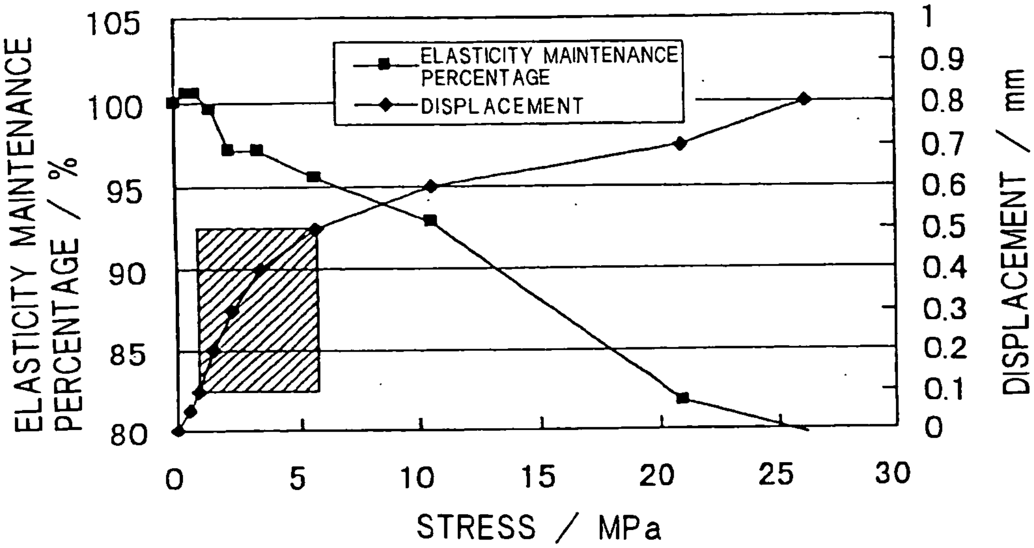
ELECTROLYTE SOLUTION
14
21

[Fig.4]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90
85
80
ELASTICITY MAINTENANCE PERCENTAGE
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0.7
0.6
0.5
0.4
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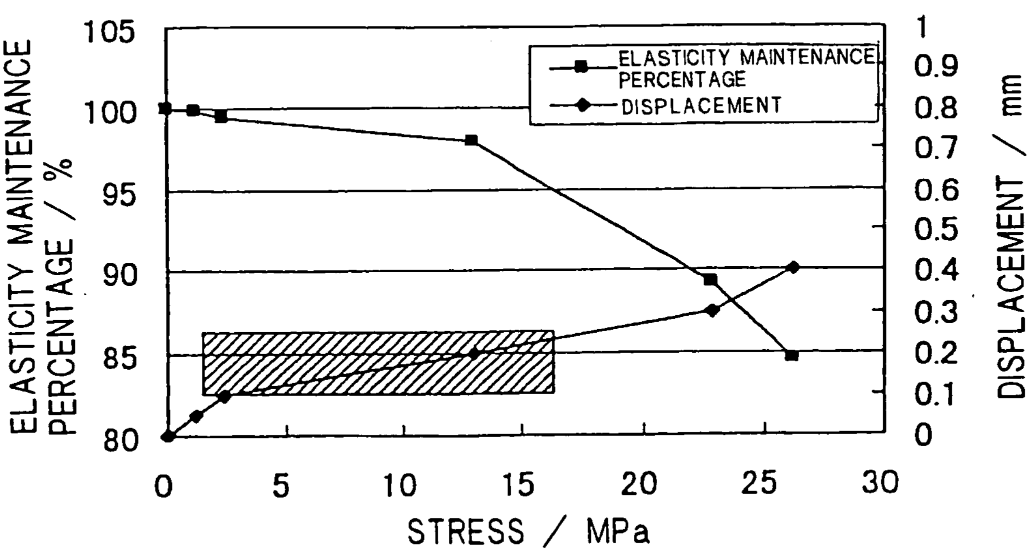
STRESS / MPa

(a)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DISPLACEMENT / mm
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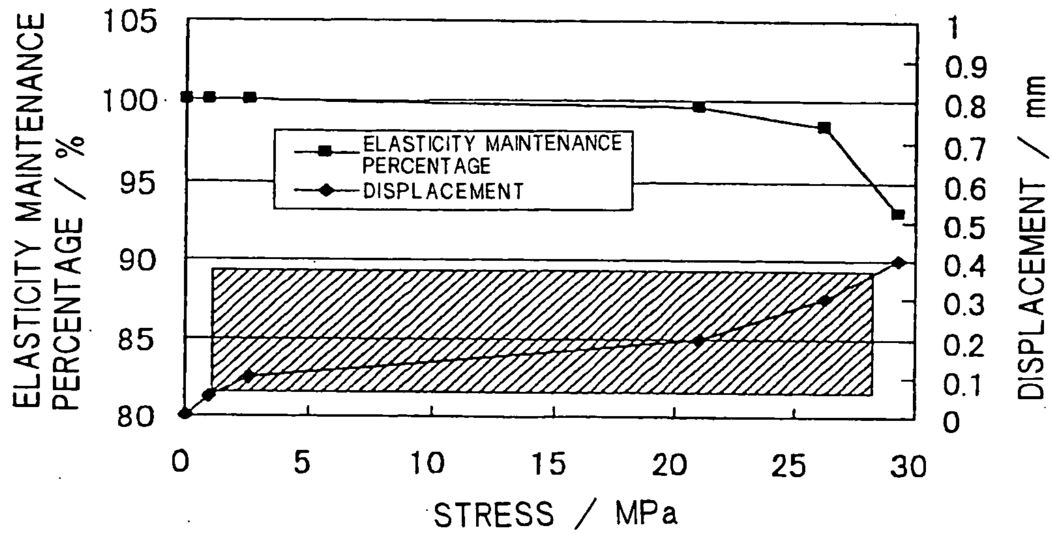
STRESS / MPa

(b)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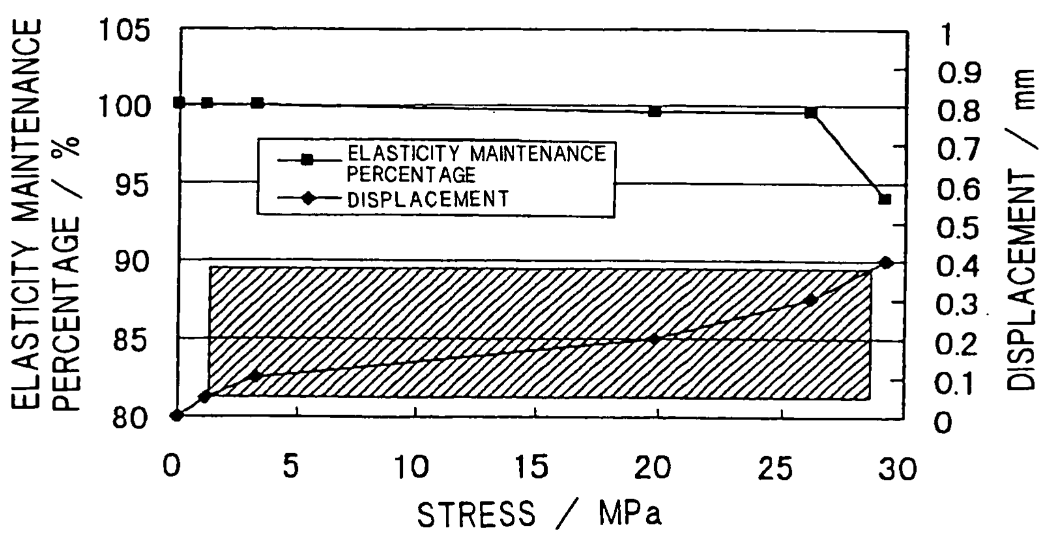
ELASTICITY MAINTENANCE PERCENTAGE
DISPLACEMENT

(c)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DISPLACEMENT / mm
ELASTICITY MAINTENANCE PERCENTAGE
DISPLACEMENT

(d)